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Introduction

Combustion chamber deposits (CCD) in internal combustion engines have been studied by various techniques to understand the relationship of performance degradation with deposit quantity and structure. XPS, XAS, NMR, and elemental analysis have offered insight into the bulk structure of C, H, N, O and metal components. MS has offered some information about compound structure, but results are limited due to the insolubility and complexity of the materials. Recently, we have reported on the metal structure by XPS and XAS of several deposits from a GM 3800 engine generated using a standard fuel and one that contains low levels of the gasoline anti-knock additive, MMT. Here we report the initial findings on the carbon structure of these deposits determined by ESI-TOF-MS and MADLI-TOF-MS.

Methods

One set of CCD samples was taken from a 6-cylinder GM 3800 engine that was operated for 200 h on a standard fuel. The other corresponding set was taken from the same engine after it was cleaned and then operated on the standard fuel containing approximately 12 ppm MMT for 200 h. The samples were soxhlet extracted with a 92 % methylene chloride/ 8% methanol (vol/vol) mixture. The solvent was removed from both fractions. The soluble fraction was dissolved in a methylene chloride/methanol mobile phase and analyzed by ESI-TOF-MS in positive ion mode. The insoluble fraction was analyzed by MADLI-TOF-MS slurried in methanol, but using no matrix. Infrared analysis was performed on both fractions as KBr pellets.

Preliminary Data

IR analyses of the whole deposits show a combination of alkyl and aromatic hydrocarbon features (regions around 2900 and 1600 cm^{-1}) and carbonyl functionality (1600 to 1700 cm^{-1}). The separated fractions show the soluble fraction to have prominent aliphatic and aromatic components with carbonyl functionality, while the insoluble fraction displays prominent carbonyl features and less aromatic features. Little differences are seen among the samples by IR.

The soluble fraction of cylinder 1 deposits from standard fuel operation was examined by ESI-TOF-MS from m/z 200 to 2000. The spectra clearly show several mass series over the entire m/z range. Each component of the series appears to be separated by m/z 72 from the next in the series, much like a hydrocarbon homologous series is separated by m/z 14. Four of these series can be clearly identified with the most intense mass of each of the series being m/z 545.41, 717.575, 601.446, and 703.549, respectively. Examining the region between m/z 545 and 617, peaks are visible at m/z 559, 573, 601,

and 615, all components of other definable mass series where the components are separated by m/z 72.

The insoluble fraction of cylinder 2 deposits from MMT fuel operation was examined by MALDI-TOF-MS. Almost no peaks are seen in the m/z range above 300. Four homologous series (separated by m/z 14) were prominent in the m/z range of 100 to 300, with many homologous series visible slightly above the base line. These four series have maxima at m/z 258, 248, 184, and 158. MS/MS of the ion at m/z 248 (248.16) shows prominent peaks at m/z 216, 156, and 142.

The IR results indicate both fractions have high concentrations of carbonyl functionality. The MS of the soluble fraction indicates possible C bonded to O species. However, N species can not be ruled out.